Exposure assessment of professional pesticide users during treatment of potato fields

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Abstract: In this study four different mixing/loading and application practices in potato fields were monitored for exposure of operators to pesticides. Each operation – mixing, loading, and application – was measured individually in order to assess its relative contribution to the total exposure value. Inhalation exposure was measured by trapping the pesticides with a sorbent tube while sampling the air around the operator's face. Dermal deposition, which was measured by means of cotton gloves on the hands and by attaching patches to the operator's clothing, was the main contributor to the total exposure. Dermal deposition on the hands during mixing and loading exceeded all other dermal values. The experimental results are compared with the results obtained by the exposure assessment model PHED V1.1. This model gives an underestimation of the levels of operator exposure during mixing, loading and application.

Keywords: operator exposure; exposure modelling; dermal deposition; patches; personal air sampling

1 INTRODUCTION

Exposure to pesticides in agriculture occurs mainly during mixing, loading, and application of pesticides and during manual activities in treated crops after re-entry. Major routes of exposure are inhalation and skin absorption.[1]

For registration of pesticides, it is necessary to consider, among other factors, the risk of the worker, which depends on toxicity as well as the level of exposure per route of uptake in the body. Toxicity depends on the intrinsic properties of the compound, although the route of uptake and the bioavailability can have some influence. The level of exposure is also affected by the properties of the compound, but mainly by the type of work and hygienic behaviour of the worker. On the basis of this assumption, modelling of worker potential exposure has been suggested as a basis for the estimation of surrogate data that may be used in a first step for risk assessment.[2]

The worker exposure models that are used for estimation of exposure have been based on different, largely unpublished, exposure studies, with various protocols. Therefore, to obtain a harmonized approach, all the studies performed in this paper, for assessing dermal and inhalation exposure, were based on the same protocols.

The human exposure assessment values in this study are obtained following a Guidance Document for the conduct of studies of occupational exposure to pesticides during agricultural applications.[3] The exposure values are used to validate the North American model.[4] The benefit of this model is that all data have been compiled in a computerized database, from which a very detailed selection can be made. In this way, the exposure can be estimated by the model by using criteria similar to those used in the sampling campaigns.

2 MATERIALS AND METHODS

2.1 Location

The trials were conducted in potato fields at two different locations in Belgium, Heurne (East-Flanders) and Rumbeke-Beitem (West-Flanders). The spray activities were conducted on 3, 15 and 30 July and 13 August 1997. The meterological conditions, the field characteristics and data on products and application techniques can be found in Table 1.

2.2 Experiments

2.2.1 Personal sampling

The workers were monitored during mixing and loading and during the application of the spray liquid. During mixing and loading only hand and inhalation exposure were monitored because these are by far the most important exposure routes involved in this activity.[1] Hand exposure was monitored by means of cotton gloves. Before mixing and loading began, the workers were asked to wash their hands intensively. Contact between the hands and other parts of the body was avoided. After loading, the gloves were removed by an assistant, imme-

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(*Received 30 March 1998; revised version received 2 June 1998; accepted 18 November 1998*)

Table 1. Field characteristics, mixing, loading and application data and meterological conditions of trials 1 to 4

	1	*2*	*3*	*4*
Location	Heurne	Rumbeke-Beitem	Rumbeke-Beitem	Rumbeke-Beitem
Date	3 July 1997	15 July 1997	30 July 1997	13 August 1997
Area (ha)	8.1	1.5	1.5	1.5
Av crop height (m)	0.65	0.65	0.65	0.70
Av inner row crop distance (m)	0.50	0.30	0.30	0.30
Av row distance (m)	0.80	0.75	0.75	0.75
Soil	Sand-loam	Sand-loam	Sand-loam	Sand-loam
Product(s)	Tattoo C	Shirlan Pirimor	Shirlan	Shirlan
Formulation type	SC	SC WG	SC	SC
Active ingredient	Chlorothalonil	Fluazinam Pirimicarb	Fluazinam	Fluazinam
AI content (g litre^{-1}) (g kg^{-1})	375	500 500	500	500
Quantity used (litre) (kg)	28.6	0.33 0.33	0.33	0.33
Spray volume (litre)	3200	500	500	500
Mix/load time (min)	Not measured	21	7	7
Appl type	Tractor-mounted hydraulic boom sprayer	Tractor-mounted hydraulic boom sprayer	Tractor-mounted hydraulic boom sprayer	Tractor-mounted hydraulic boom sprayer
Boom length (m)	27	21	21	21
No nozzles	54	42	42	42
Nozzle type	XR (cone ϕ 0.6 mm)	ALBUZ (cone)	ALBUZ (fan)	ALBUZ (cone)
Cab type	Closed cabin with air filter	Half-open	Half-open	Half-open
Tractor speed (km h^{-1})	7	4	4	4
Spray pressure (bar)	2.6	3.5	3.2	3.5
Appl time (min)	55	23	19	20
Atm pressure (hPa)	1008	1014	1008	1012
Av air temp. (°C)	20	23	23	25
Av RH of air (%)	60	84	84	66
Wind direction	S	W	SW	W
Av wind speed (m s^{-1})	4	4	1.5	5
Precipitation	None	None	None	None

diately extracted with an appropriate solvent and stored in a cool, dark box.

Inhalation exposure was measured with a personal air sampling (PAS) pump (Gilair 3). A glass tube was connected to the PAS pump with flexible tubing. The 10-cm glass tube (10 mm in diameter) contained a 20-mm section of sorbent (analytical layer) and a 10-mm section of sorbent (control layer). Between both layers and at both ends a plug of silanized glass wool was inserted. The sorbent Amberlite XAD_2 (Rohm & Haas) was chosen because of our previous experimental experience.[5]

The pump was calibrated by means of a GILIAN Diagnostic Calibrator to 1.5 litre min^{-1} (accuracy 5% of scaling). This rate was chosen in accordance with component breakthrough properties.

In order to evaluate the potential dermal exposure during the application of the spray liquid, the patch method was used. Patches, 5 mm thick, consisting of four layers of respectively gauze, cellulose, polyethylene and wrapping paper[6] were attached to the workers' clothing. The positions of the patches are given in Table 2.

The samples, 49 cm^2, were immediately extracted in an appropriate solvent, analysed and the results calculated in terms of the appropriate body surface area in accordance with EPA convention (Table 2).[7]

Hand exposure and inhalation exposure were monitored as described above. The seat and steering wheel of the tractor were cleaned in order to avoid accidental contamination.

2.2.2 *Blanks*

Before each application took place, blank samples were taken in the area where mixing and loading occurred (air sample, 15 min) and in the field (air sample, 30 min). The solvents used for extraction, patch blanks and blank samples of cellulose strips were also checked.

Table 2. Surface areas for regions of adult body and location of dermal exposure patches

Region of body	*Surface area*[a] (cm^{-2})	*Location of patches*
Head and face	1300	Front of cap
(Face)	650	
Back of neck	110	Back
Front of neck (includes "V" of chest)	150	Chest
Back	3550	Back
Chest/stomach	3550	Chest
Upper arms	2910	Each upper arm
Forearms	1210	Each forearm
Upper legs	3820	Each thigh
Lower legs	2380	Each lower leg (shin)
Feet	1310	Each foot or sock
Hands	820	Absorbent glove

[a] Surface areas include both arms, both legs, both hands

2.2.3 Field recovery

In order to evaluate field recoveries and in order to determine pesticide losses due to storage, transit conditions and exposure to light, three blank samples of each matrix were spiked with an appropriate amount of pesticide standard and treated similarly to field samples (exposure to sunlight, storage in cooling container for 8 h). For the field recovery of the air samples an appropriate amount of pesticide standard was directly injected into the air sampling glass tube and 90 litres air was drawn through the XAD_2 layers (1 h at 1.5 litre min^{-1}).

2.3 Extraction

The patches, gloves and cellulose strips were cut into small squares (approx. 1 × 1 cm), placed into a 250 or 500 ml recipient and immersed in an appropriate solvent: hexane was used for the extraction of chlorothalonil, fluazinam and pirimicarb.

At the laboratory of samples were placed in an ultrasonic bath for 30 min. After Büchner filtration the samples were placed in a rotavapor until almost dry and redissolved in an adequate amount of solvent. The air samples were extracted in 10 ml of solvent and placed in an ultrasonic bath for 30 min.

2.4 Gas-liquid chromatographic analysis

Standard solutions and analytical samples (2 µl) were injected into the gas-liquid chromatograph. Table 3 gives the gas-liquid chromatography conditions.

2.5 Estimating worker exposure

The Pesticide Handlers Exposure Database (V1.1)[4] is a generic database containing measured exposure data for workers involved in the handling or application of pesticides in the field. This database was designed by a task force consisting of representatives from Health Canada (HC), the US Environmental Protection Agency (EPA), and American Crop Protection Association (ACPA). The software was developed by Versar, Inc.

This database enables predictive exposure assessment based on statistical analysis of existing exposure data. The circumstances for which exposure has to be assessed can be defined by creating a subset of files meeting certain criteria. Exposure data obtained by PHED were compared to the results of this study.

Table 3. Gas-liquid chromatography conditions

Active ingredient	*Chlorothalonil*	*Fluazinam*	*Pirimicarb*
Column packing	5% OV 101	5% OV 101	3% OV 17
Column length (cm)	50	50	50
Detector	ECD	ECD	TSD
Temperature (°C)			
injector	200	200	230
oven	180	200	200
detector	300	300	250
Retention time (min)	1.2	3.5	1.2

3 RESULTS AND DISCUSSION

3.1 Field recovery and limit of detection

Losses during field treatment due to storage and exposure to sunlight are expressed as field recovery. The field recoveries and the limit of detection for the pesticides and matrices included in the study are shown in Table 4. The recoveries obtained with the pesticide formulations were similar.

3.2 Personal sampling

3.2.1 Exposure during mixing and loading

Data for potential inhalation exposure and the pesticide residues retained by the hands from the mixing and loading process are shown in Table 5. Because different quantities of active ingredients were applied, potential exposure results were normalized in order to allow comparison of the exposure figures from the different trials. The results (Table 5 and 6) are thus expressed in µg kg^{-1} AI.

Table 4. Field recoveries and limit of detection for the pesticides and matrices used in the study

	Patches	*Cotton gloves*	*Air samples*
Field recovery (%)			
chlorothalonil	102.1	100.3	–
fluazinam	96.1	98.0	95.2
pirimicarb	100.8	94.7	87.3
Limit of detection			
chlorothalonil	0.03[a]	0.001[b]	–
fluazinam	0.04[a]	0.004[b]	0.004[c]
pirimicarb	0.05[a]	0.003[b]	0.007[c]

[a] ng cm^{-2}
[b] µg per glove
[c] µg per tube

Trial	Active ingredient	Hand, right (μg kg^{-1} AI)	Hand, left (μg kg^{-1} AI)	Inhalation (μg kg^{-1} AI)
1	Chlorothalonil	–[a]	–	–
2	Fluazinam	317.96	362.46	1.26
	Pirimicarb	129.88	331.56	37.89
3	Fluazinam	153.29	127.19	9.76
4	Fluazinam	132.93	242.63	0.58

[a] Not measured

Table 5. Hand exposure and inhalation exposure of the workers from mixing and loading during the different trials

The potential operator exposure due to inhalation was similarly expressed as μg kg^{-1}. The breathing rate of an average human being is 1.74 m^3 h^{-1},[1] so the potential inhalation exposure (PIE) was calculated using the following equation:

$$\mathrm{PIE} = 1.74ct/m$$

where

c = measured aerial concentration of pesticide, (μg m^{-3})

t = time of exposure (h)

m = mass of AI handled (kg).

In this study cotton gloves were used for measurement of potential dermal exposure to the hands. Davis[8] indicated that the use of cotton gloves gives an overestimation of exposure because they may absorb more material than would be retained by the skin. Alternative methods of direct measurement involve washing pesticide deposited on bare hands. The major factors for the decision to use cotton gloves were the fact that they can be changed very quickly and that they provided some degree of safety for the operators, especially when using solid formulations.

It should be noted that the same mixing and loading strategies were applied in trials 2 to 4. The worker was right-handed. Mixing and loading were always done in the same little room. The worker from trials 2 to 4 first made a primer tank mixture in a bucket (10-litre) which was further diluted in the tank.

The potential exposure values in Table 5 show clearly the correlation between the hand exposure and the amount of active ingredient handled. Potential inhalation exposure was rather small compared to the hand exposure. Table 5 indicates clearly that a solid formulation (pirimicarb WG) gives rise to a much higher potential inhalation exposure than a liquid formulation (fluazinam SC) does.

3.2.2 *Exposure during application*

The application technique was in all cases the same: a tractor-mounted hydraulic boom sprayer. However, there were some differences in application pressure, number of nozzles and nozzle type, tractor velocity and cabin type (Table 1), the latter being the most direct factor influencing exposure. Application 1 was conducted in a closed cabin equipped with carbon filter, while applications 2 to 4 were conducted in a half-open cabin: the rear side of the cabin was open. Dermal deposition was measured by the use of cotton gloves on the hands and patches attached to various parts of the operator's clothing (Table 6).

The dermal deposition levels of trial 1 (not the hands) are 5 to 130 times lower than the dermal deposition levels of trials 2 to 4 (Table 6). Thus the use of a closed cabin equipped with carbon filter (sampling campaign 1) is effective in reducing

	Potential exposure (μg kg^{-1} AI)				
	Chlorothalonil (1)	Fluazinam (2)	Pirimicarb (2)	Fluazinam (3)	Fluazinam (4)
Head and neck	0.78	24.97	13.95	19.76	63.98
Back	1.39	54.85	57.13	181.14	78.46
Chest/stomach	1.39	46.64	130.18	24.49	27.48
Upper arms	1.04	38.9	34.35	18.67	26.92
Lower arms	0.39	9.76	13.25	7.95	6.68
Thighs	5.49	47.54	28.71	150.96	29.56
Shins	3.11	30.04	37.7	40.01	48.65
Hands	81.58	225.87	209.28	3.9	21.81
Inhalation	–[a]	1.38	1.4	7.46	1.2

[a] Not measured

Table 6. Dermal and inhalation exposure during application from trials 1–4

	Mixing and loading		Application	
	Inhalation exposure ($\mu g\,kg^{-1}$)	Dermal deposition ($\mu g\,kg^{-1}$)	Inhalation exposure ($\mu g\,kg^{-1}$)	Dermal deposition (less hands) ($\mu g\,kg^{-1}$)
Chlorothalonil (1)	–[a]	–[a]	–[a]	13.59
Fluazinam (2)	1.26	680.42	1.38	252.7
Pirimicarb (2)	37.89	461.44	1.4	315.27
Fluazinam (3)	9.76	280.48	7.46	442.98
Fluazinam (4)	0.58	375.56	1.2	281.73

Table 7. Total operator exposure for mixing and loading and application

[a] Not measured

dermal exposure. Hand exposure during trial 1 is relatively high in comparison with the dermal exposure of the other parts of the body. This is due to the fact that the operator did not wash his hands very well after the mixing/loading procedure.

Table 7 shows the total potential operator exposure due to inhalation and dermal exposure for mixing, loading and application (no hands). Hand exposure is omitted from the calculation of the total dermal exposure during application because the washing procedure of the hands after mixing and loading had been too variable. In trial 1 there was no information on the hand washing after mixing and loading, in trial 2 the operator washed his hands with only water and in trials 3 and 4 the operator washed his hands with soap and water.

Comparison of dermal exposures for mixing and loading and application indicates that the hand exposure during mixing and loading is comparable with the total dermal exposure during application. The dermal exposure during mixing and loading and application (less hands) is 12 to 648 times higher than the inhalation exposure during these two activities.

The dermal exposure (less hands) during the application of trial 1 is 18 to 33 times lower than those of the trials 2 to 4, due to the use of a closed cabin equipped with air filter.

3.3 Estimating worker exposure

The experimental results of the different trials were compared with the results obtained by PHED modelling (Table 8). For estimation of exposure during mixing and loading, two different scenarios were followed, taking into account the different formulation types used. For scenario 1, the exposure during the mixing and loading of pirimicarb (Pirimor) was simulated. The mixing and loading of fluazinam (Shirlan) was simulated in scenario 2. From the PHED mixing-loading file (MIXLD.FILE) two subsets were created by imposing the next criteria:

scenario 1: solid type 'dry flowable'
packaging type 'bag'
scenario 2: liquid type 'aqueous suspension'
packaging type 'bottle'

For the estimation of exposure during application, again two scenarios were used. The differences in the two scenarios were the use of a closed cabin in strategy 3 (for comparing with trial 1) and the use of an open cabin in strategy 4 (for comparing with trials 2 to 4). From the PHED application file (APPL.FILE) two subsets with the following criteria were created:

strategy 3: cab type 'closed cab/window closed' or 'closed cab/window closed/filt air' application method 'groundboom tractor'

	Estimated exposure ($\mu g\,kg^{-1}$)			
	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Head and neck	–[a]	–	0.34	3.55
Back	–	–	1.21	14.74
Chest/stomach	–	–	1.93	14.16
Upper arms	–	–	1.4	13.48
Lower arms	–	–	0.45	7.03
Thighs	–	–	2.42	20.88
Shins	–	–	1.11	13.84
Hands	21.01	1019.06	1.66	14.35
Total dermal (less hands)	–	–	8.86	87.68
Inhalation	1.84	0.41	0.1	1.63

Table 8. Exposure assessment by PHED-modelling for the different scenarios

[a] Not calculated

strategy 4: cab type 'open cab' or 'closed cab/ window open'
application method 'groundboom tractor'

No further criteria were imposed in these four scenarios in order to keep enough records within the selected datasets for statistics. Potential exposure was calculated (no clothing). Actual and estimated head patches were used to calculate potential exposure. Potential inhalation exposure was calculated for a rate of 29 litre min^{-1} (average labour). The values were also normalized ($\mu g\,kg^{-1}$ AI applied).

As all the values (except for head and neck of scenario 3) were log-normal distributed, the geometric mean is the best value to use for comparison with our results. The result for head and neck of scenario 3 followed a different (not defined) distribution, so the median value was used for comparison.

The results of scenario 1 are much lower than the experimental results obtained in the mixing and loading of pirimicarb (Table 7). The inhalation exposure in trial 2 for pirimicarb is 21 times higher than the estimate obtained by the PHED model, while the hand exposure during mixing and loading of pirimicarb is 22 times higher than the PHED estimate.

The assessment of inhalation exposure in scenario 2 (mixing and loading of fluazinam) turned out to be lower than the experimental values (Table 7). The hand exposure during mixing and loading of fluazinam is slightly (1.5 to 3.5 times) overestimated by the PHED-model (Tables 7 and 8).

The values obtained in scenario 3 seemed to be rather a good estimate (except for hands) of the experimental results of trial 1 (Tables 6 and 7). The experimental hand exposure is rather high, probably due to fact that chlorothalonil is not well washed off after the mixing and loading and is absorbed by the cotton gloves during the application.

The experimental results of potential dermal exposure during application in trials 2 to 4 are higher (up to 18 times) than the values estimated by scenario 4 (Table 6). The hand exposure of trial 2 exceeds that of trial 4 and the estimated value by more than 10-fold.

Some critical remarks have to be made. A worker exposure model is as good or as bad as the underlying data-base. This indicates the need for 'good' data obtained with validated techniques for assessment and analysis. The data-sets used in the PHED model were not obtained by the use of a uniform method for the assessment of human exposure to pesticides. Therefore the variation of exposure due to the different methods, and also due to differences in the field, is large. Even in this study there is sometimes a great variation in the exposure of the same body part (Table 6). Batel *et al*[9] have shown that the actual exposure of, for instance, the worker operating a spray directed downwards also depends on the size and height of the spray boom above the crop and the distance between it and the worker as well as on the difference in height between the boom and his seat on the vehicle. This means that the choice of a statistical parameter (geometric mean, arithmetic mean, median) to estimate exposure levels is not always easy and frequently leads to large differences in the estimated value.

One must also take into account that, for the PHED estimation of exposure values in this study model, the scenario circumstances were not identical to the different trials studied in the field. This is due to the fact that the created subset would otherwise be too small to give a statistically acceptable estimation of the exposure.

4 CONCLUSIONS

The spraying operations reported here represent actual spraying practice. The different trials show clearly that the inhalation exposure is much lower than the potential dermal exposure. Inhalation exposure during mixing and loading of an aqueous suspension (liquid formulation) is much lower than of a wettable granule (solid formulation). There is also a difference in exposure between the use of a half-open cab unit and a closed cab unit with air filter. Charcoal-filtered air-intake units minimize exposure while maintaining comfort.

Comparison of the values obtained in this study and the values obtained by the PHED model for estimating potential operator exposure indicates that the estimated values are in almost all scenarios lower than the experimental results. It must be clear that these values are based on very variable data, and therefore great differences between exposure levels are possible. The differences between the experimental values and the PHED estimations can be explained partly by the statistical treatment chosen for the exposure assessment and partly by the differences in field conditions between North America (PHED data-base) and Belgium (experimental data). This should lead to a careful and conservative use of this model for the assessment of pesticide exposure in Belgium.

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